Semiconductor Electrodes

VI. A Photoelectrochemical Solar Cell Employing a TiO$_2$ Anode and Oxygen Cathode

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ABSTRACT

A photoelectrochemical cell for conversion of light to electrical energy based on the photosensitized oxidation of water at a chemically vapor deposited, thin film, n-type TiO$_2$ anode and the reduction of oxygen at a fuel cell-type cathode is described. The effect of load resistance on the current, cell voltage, and power was studied, and quantum and power efficiencies under short-circuit conditions for monochromatic light of about 365 nm was estimated as 26% and 1-2%, respectively. Open-circuit cell voltages of 0.89V were obtained. The cell is simple to construct and is capable of continuous operation with no apparent deterioration in performance.

Photoeffects at semiconductor electrodes received renewed attention when these materials were recognized as potential candidates for use in the conversion of light to electrical and chemical energy via some electrochemical process; this subject has been reviewed and discussed recently (1, 2). Of special interest are semiconductor electrodes which do not decompose or corrode during the photoelectrochemical process (*e.g.*, n-type TiO$_2$), so that the light exclusively induces charge transfer to selected species in solution. We describe here the construction and behavior of an electrochemical photocell which produces electrical power under illumination by light of suitable spectral characteristics. Although this electrochemical cell differs in operating mechanism from the familiar solid-state solar cell, the result, conversion of light to electrical energy, is the same. The cell is based on the photosensitized oxidation of water to oxygen at a chemically vapor deposited n-type TiO$_2$ anode and the reduction of oxygen at a fuel cell-type cathode and offers good quantum efficiency, simple construction, and continuous operation without renewal of electrolyte or electrode decomposition. Its major limitation for utilization of solar energy is its response only to the short wavelength (below 400 nm) portion of the spectrum.

Experimental

The cell, shown schematically in Fig. 1, consisted of an aqueous solution (acidic or basic) confined between a quartz window and the cathode. The cathode was the type employed in hydrogen-oxygen fuel cells (American Cyanamid experimental fuel cell electrode, 2.5 mg Pt/cm^2, deposited on a nickel-gold screen with Teflon backing). In parallel and spaced 12 cm away was fixed a bright Pt foil (0.2 mm thick) which was perforated by numerous pinholes (about 6 holes/cm^2) which reduced its geometric area only slightly and which was covered on both sides with a TiO$_2$ film produced by chemical vapor deposition (CVD) (3). The side facing the window served as the photoactive TiO$_2$ anode with ionic conductivity from this part of solution to the oxygen electrode being accomplished through the pinholes in the foil. The TiO$_2$ film on the other side of the membrane (facing the O$_2$ electrode) eliminated contact between solution and bare Pt surface. The procedure for the CVD of the TiO$_2$ film described by Hardee and Bard (3) was followed. The Pt substrate, after being punched, was cleaned in a 3:1 HCl:HNO$_3$ mixture; the film was then deposited and annealed. After about four successive coatings, each of them at the maximum thickness possible without

causing the film to peel off, the resulting film was quite thick. It had a hazy gray appearance and interference fringes could no longer be observed; the adhesion of this film to the Pt was excellent. After the CVD the TiO$_2$ film was vacuum treated for 8 hr (750°C, 10^{-4} Torr). This procedure converted the dielectric TiO$_2$ film into a conductive n-type material.

Two inlets to the cell allowed the immersion of a saturated calomel reference electrode (SCE) and another Pt electrode into the cell for potentiostatic measurements. For these a Princeton Applied Research (PAR) Model 173 potentiostat was used. While operating as a galvanic cell, the voltage and current were determined with a standard resistance load connected across the cell terminals. A 450W Xenon lamp (Oriel Corporation, Stamford, Connecticut) was the light source. For spectral response and efficiency determinations an Oriel Model 7242 high intensity grating monochromator and a Model 550 (EG & G, Salem, Massachusetts) calibrated radiometer assembly were used.

Results and Discussion

Electrochemical photocells can be classified as two distinct types (1, 2). In the first, radiation is converted into chemical energy, *i.e.*, under illumination a normally endothermic chemical reaction will take place spontaneously or with an electrical energy input less than the reversible value for this reaction. In the second type, which is the one of interest here, no over-all chemical change occurs in the system and the absorption of light results in the generation of electrical power. Both electrochemical half-cell reactions which were
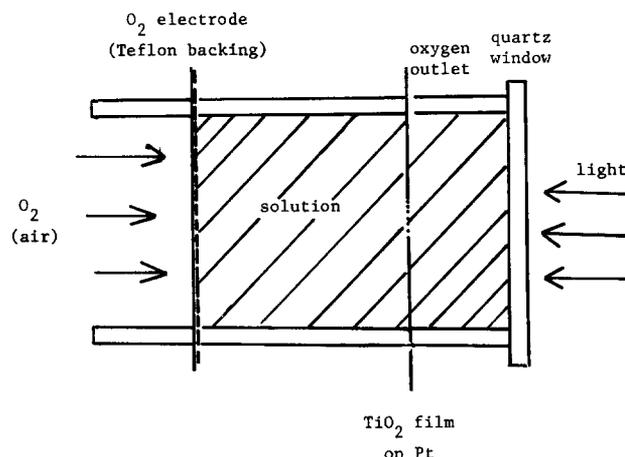
Fig. 1. Schematic representation of the n-TiO$_2$/Pt(O$_2$) photoelectrochemical solar cell.

employed have been the subject of separate previous studies and so are not dealt with here in detail. The anode reaction was the evolution of oxygen at an illuminated n-type TiO_2 electrode. This reaction has been studied at both single crystal (4-7) and thin film (3) materials. With the omission of mechanistic details oxygen evolution from aqueous solution at an illuminated TiO_2 electrode can be represented as

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \qquad \text{(acidic solution)} \quad [1]$$

$$4\,OH^- + 4h^+ \rightarrow O_2 + 2H_2O \qquad \text{(basic solution)} \quad [2]$$
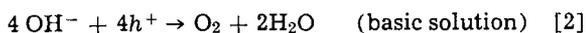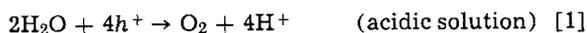
The holes (h^+) are produced by the appropriate bandgap illumination and the efficiency of the process depends on the electrical state of the semiconductor electrode. A sufficiently positive bias will result in an extended space charge region in which the recombination of the photogenerated holes with electrons (e^-) (the majority carrier) is minimized and an efficient separation of the photoproduced h^+/e^- pairs occurs, with the holes drifting to the electrode surface. The photooxidation of water takes place at a "negative overpotential" (8), *i.e.*, at a less positive electrode potential than the reversible one (thermodynamically independent of electrode composition), thereby allowing the utilization of the light energy. The cathode reaction, the well-known reduction of oxygen at a Pt catalyst fuel cell electrode

$$O_2 + 4H^+ \rightarrow 4e^- + 2H_2O \qquad \text{(acidic solution)} \quad [3]$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^- \qquad \text{(basic solution)} \quad [4]$$
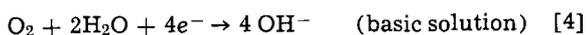
is just the reverse of the anodic reaction, except that electrons participate in it instead of holes.

The behavior of the complete cell can be predicted from the individual current-potential curves for each electrode measured potentiostatically against a reference electrode; typical results for $5M$ NaOH and $5M$ $HClO_4$ solutions are given in Fig. 2. If the electrodes are shorted together (load resistance R_L, of 0) and solution resistive drop is negligible, they attain the same potential, at which the current at each is of the same magnitude and opposite in polarity (dashed line, Fig. 2). The less favorable situation in the acidic solu-

tion results from the less reversible behavior of the oxygen cathode, *i.e.*, its failure to shift to more positive potentials with decreasing pH by an amount equivalent to the anode shift (for a reversible reaction a shift of 60 mV/pH unit is expected). The open-circuit potential in alkaline solution is about 900 mV under illumination. The maximum current ($R_L = 0$) is about 85% of the saturation (plateau) current which represents the maximum current obtainable at a given light level for the photooxidation process at the TiO_2 electrode. Thus, even if the cathode could be shifted to more positive potentials [*e.g.*, at a silver/silver oxide cathode (9)] the maximum cell current would only increase by a small amount; the cell power would increase, however, because of the greater cell voltage. During operation oxygen is evolved at the TiO_2 electrode and the same amount of oxygen is incorporated from outside of the cell at the oxygen electrode. Because of the high concentration of reactant employed (water, OH^-, O_2), concentration polarization is negligible. A small outlet near the upper part of the TiO_2 electrode allowed escape of the electrogenerated oxygen. The solution on the dark side of the Pt/TiO_2 electrode was held at a pressure slightly greater than atmospheric so that the solution level remained constant throughout the cell.

The voltage, current, and power curves of the cell for different R_L values at the same light levels as in Fig. 2 are given in Fig. 3. In bright sunlight about one-half to one-third of the power shown in Fig. 3 was obtained. The internal resistance of the cell was mainly due to that of the TiO_2 film, estimated to be 5-10 ohms. At the current density employed, little power dissipation due to internal cell resistance was observed. The spectral response of the TiO_2 film agreed with that of previous reports (3, 7, 10) with a maximum at about 365 nm (uncorrected for lamp output). The quantum or photon efficiency, n_ϕ (1), defined as the current density at the TiO_2 electrode divided by the flux of light at the wavelength of maximum response (or electrons flowing per photon impinging on electrode), determined under potentiostatic conditions for the saturation current, was $30 \pm 5\%$. This figure should be regarded only as a representative one, since different TiO_2 films differ in their photoresponse depending on the method and conditions of preparation. A single crystal of TiO_2 was found to have an efficiency of $80 \pm 10\%$, under similar conditions. Thus, if the film was sufficiently thick for the absorption of all the light, some other factors, such as enhanced surface e^-/h^+ recombination, may contribute to the lower efficiency of the TiO_2 films. In the operation as a galvanic cell with $R_L = 0$ about 85% of the saturation current is obtained for the same illumination condi-

Fig. 2. Current-potential curves of the cell electrodes. (a) TiO_2 film electrode, $5M$ NaOH, under illumination and (a') in dark; (b) TiO_2 film electrode, $5M$ $HClO_4$, under illumination and (b') in dark; (c) oxygen cathode in $5M$ NaOH; (d) oxygen cathode in $5M$ $HClO_4$. Electrode areas, 20 cm². White (Xe) light illumination.
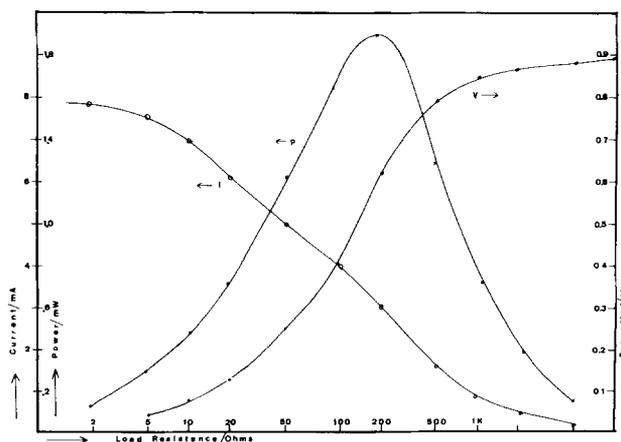
Fig. 3. Voltage (V), current (I), and power (P) of the cell as function of the load resistance. Under same white (Xe) light intensity as in Fig. 2.

tions. Thus the quantum efficiency under short-circuit conditions is about 26% for this cell. The maximum power efficiency takes into account the energy of the incident photons as well as their flux and depends on R_L. It will be defined as the maximum cell power per square centimeter electrode area over the light intensity at the wavelength which corresponds to the maximum response. This quantity could not be measured directly, because of the low intensity of the monochromatic light (produced using a slit width of about 2 mm to give a bandwidth of about 2 nm) resulting in an electrical power of less than 1 μW. Moreover, this power efficiency depended on the illumination intensity and R_L. If the white light intensity was varied, using neutral density filters in the ratio of 1:0.62:0.40:0.12, an over-all (polychromatic) maximum electrical power with a ratio of 1:0.6:0.46:0.15 at loads of 150, 200, 500, and 1000 ohm, respectively, was obtained. The corresponding saturation currents at the TiO_2 measured potentiostatically were, as expected, linear with white light intensity and were 10, 6.1, 4.1, and 1.2 mA for the intensity ratios given above. These observations are consistent with the fact that in general the current at the TiO_2 electrode is not exactly proportional to the light intensity at all potentials on the rising portion of the wave as it is for the saturation current. The maximum (monochromatic) power efficiency was estimated as follows. The cell power (0.22 mW/cm²) and the TiO_2 potentiostatic saturation current (1.5 mA/cm²) were measured under the same intensity white light concentrated on the center 1 cm² of the electrode. Then, using monochromatic light, the light intensity (96.4 μW/cm²) and saturation current for the TiO_2 (9 μA/cm²) were determined. Thus, for monochromatic light (367 nm) a saturation current of 0.093 μA/μW is produced. The saturation current found with the white light is thus equivalent to a monochromatic light intensity of 16 mW/cm². Thus the maximum power efficiency for monochromatic light is 1-2%. The efficiency for solar energy conversion is much lower, of course, because only about 3% of the solar spectrum would be utilizable at a TiO_2 electrode (1).

The cell appeared capable of operation either continuously or in on/off cycles with no deterioration in performance (e.g., Fig. 4). The cell also could operate without a separate oxygen feed to the cathode (on the oxygen dissolving at the anode) or with air fed to the cathode. In the latter case the cell, besides producing energy, serves to separate oxygen from the air.
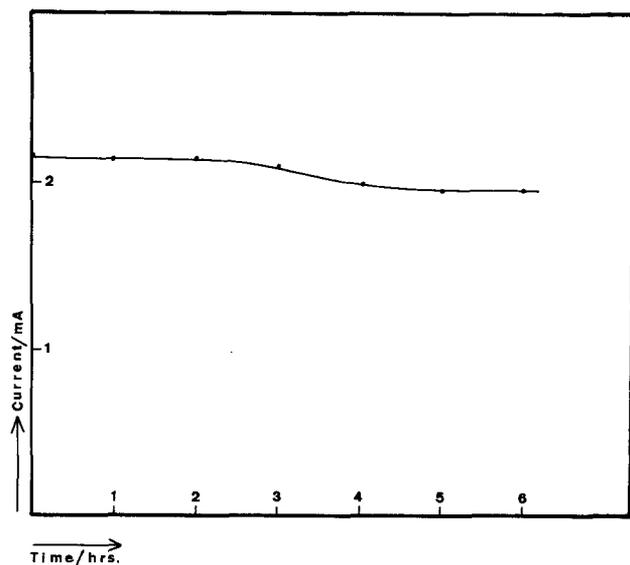
Fig. 4. Cell operation under white light illumination with time; load resistance, 100 ohms.

Although the described cell arrangement appeared satisfactory, i.e., allowed full illumination of the photosensitive surface with a reasonable current density distribution and internal ohmic losses, some other cell configurations were also tried. Among these was a thin sandwich cell employing the same oxygen cathode and electrolyte solution but with the TiO_2 film deposited on a transparent SnO_2 film-on-glass substrate. Memming (10) previously showed that such TiO_2 films show light-induced electrochemical activity and that the SnO_2 is transparent to the wavelengths which generate photocurrents at the TiO_2 film. In this arrangement the TiO_2 film faces the cathode and is illuminated from the rear through the glass plate and the SnO_2 film. In this way the cell geometry is optimized and the distance between the electrodes, volume of solution, and its internal resistance are minimized. However, this cell performance was inferior to that of the previously described one; we attribute this mainly to the poorer efficiency of the TiO_2 film deposited on the SnO_2 substrate. We found it difficult to prepare a TiO_2 film which was thick enough to give good photosensitized electrochemical behavior and show good conductivity and at the same time obtain good light transmittance through the glass/SnO_2/TiO_2 system. The major problem was that the glass substrate system could not be subjected to the high temperatures needed in the CVD-coating procedure without deterioration of the SnO_2 film. The conversion of the TiO_2 to an n-type material in this case was accomplished by heating to 450° in a hydrogen atmosphere, since heating to high temperatures under vacuum was not possible.

We might also note that a recent paper by Mavroides et al. (11) utilized a platinized-Pt cathode of geometric area 50 times that of the anode operating on the reduction of dissolved oxygen to evaluate the performance of various semiconducting TiO_2 anodes. High quantum efficiencies were also obtained in that study for operation in a photogalvanic mode. Similarly Keeny et al. (6) effectively used a Pt-oxygen cathode in their laboratory cell.

While the photoelectrochemical cell here operates on the water-oxygen system, similar cells for conversion of light to electrical energy without a net chemical change in the system could operate with other redox couples (represented by $Ox + ne \rightleftarrows Red$). The potential range of the TiO_2 anode would be limited to values near the flatband potential where sufficient band bending occurs to cause efficient separation of the h^+/e^- pairs. Thus for any redox couple the anodic i-E curve will probably be close to the one given for water oxidation. The cathode curve for reduction of Ox to Red will depend on the $E°$ and the reversibility of the reduction reaction. The more positive the values at which the i-E curve lies the greater will be the power of the cell at a given illumination level. Thus redox couples with more positive $E°$ values should lead to higher power efficiencies with the constraint that for couples with $E°$ values larger than that of the oxygen/water couple (adjusted to the appropriate pH value), species Ox will tend to be unstable in aqueous solutions. Moreover the work of Fujishima and Honda (12, 13), as well as our own recent studies (14) suggest that as the $E°$ of the redox couple becomes more positive water may compete more successfully with Red for the photogenerated holes, leading to an over-all irreversibility in the cell reaction. If one abandons an aqueous system, however, and uses a solvent with a wider available potential range, such as acetonitrile, for example (15), then even more positive redox couples can be employed. The most positive $E°$ value for a couple used in a solvent which participates in neither the anodic nor cathodic reaction is one located at about the position of the valence band of the n-type semiconductor, where Red is still capable of combining with holes at the electrode surface. Under

these conditions the maximum utilization of the energy of the incident photons should occur.

Acknowledgment

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Primary Resistances for Ring-Disk Electrodes

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ABSTRACT

A system consisting of a disk electrode, a concentric ring electrode, and a large counterelectrode at infinity has three independent resistance values describing the primary potential difference between any two electrodes when current is passed between any two electrodes. These resistance values are calculated and presented as dimensionless correlations as functions of the ratios of radii of the disk and ring.

A common electrode geometry in electroanalytical and research applications involves a disk electrode and a concentric ring electrode both embedded in an insulating plane and rotated about the axis of the disk. Species produced by an electrochemical reaction at the disk can frequently be detected quantitatively by electrochemical reaction at the ring (1-3). In some of these applications it is desirable to assess the ohmic potential drop in the solution. For example, to have a controlled electrode potential for the reaction at the disk one needs to know how a current to the disk and a current to the ring separately influence the potential in the solution in the neighborhood of the disk (4, 5). To ensure that a limiting current is maintained on the ring involves a similar question (6).

Experimental efforts to answer these questions involve abrupt changes in the current to either the ring or the disk followed by a measurement of the change in potential of both the ring and the disk as shortly thereafter as possible (4, 5, 7). Such rapid changes in potential and current are associated with the primary distributions of potential and current (8).

Consequently, we can define a mathematical problem in which the potential obeys Laplace's equation

$$\nabla^2 \Phi = 0 \qquad [1]$$

the potential is zero at infinity, and has a uniform value in the solution adjacent to each electrode. Corresponding to a zero current density, the normal component of

the potential gradient is zero on the insulating annulus between the disk and the ring and on the plane surrounding the ring. This problem excludes consideration of the variation of conductivity within the thin diffusion layer adjacent to the electrodes and effectively regards the change in potential drop to be determined by the bulk of the solution. Also excluded from consideration is the effect of electrode kinetics, it being assumed that the double-layer capacity is sufficiently large that the potential difference across it does not change during the time of the measurement (8). [The course of events involving the change of the charge of the double-layer capacity has been examined by Nişancioğlu and Newman (9-11).]

The problem thus defined is limited in scope since it involves only the geometry of the system, the conductivity of the solution, and the potentials and currents themselves. The principal result of the model is the expression of the disk and ring potentials in terms of the disk and ring currents

$$V_d = R_{dd}I_d + R_{dr}I_r \qquad [2]$$

$$V_r = R_{rd}I_d + R_{rr}I_r \qquad [3]$$

where I_d and I_r are the total currents to the disk and ring electrodes, respectively, and V_d and V_r are the potentials, presumed uniform, in the solution adjacent to the two electrodes. In the absence of concentration and surface overpotentials, V_d and V_r can be regarded to be the potentials of the electrodes themselves, and this is the usual manner of speaking when discussing primary-distribution problems. Bear in mind that in